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A principle focus of this research program is the electronic structure aspects of nonadiabatic processes related to the stability and formation of high energy density materials (HEDMs). Also considered are nonadiabatic and relativistic effects that impact the detection of molecular species involved in HEDM or chemical laser development. These studies are enabled by a unique system of electronic structure algorithms, the **BROOKLYN** programs, that provide advanced capabilities for the study of the electronic structure aspects of spin–forbidden and spin–allowed electronically nonadiabatic processes. These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of electronically nonadiabatic processes. Of particular significance in this grant period has been the development of algorithms for characterizing surfaces of intersection of two states of distinct spin–multiplicity or *two states of the same symmetry*. They complement our existing capabilities for determining the relevant intersurface couplings, the derivative couplings that couple states of the same spin–multiplicity and the spin–orbit and dipolar spin–spin interactions that couple states of distinct spin–multiplicity and will be of considerable value in studying the radiationless decay of energetic species. Of particular relevance is this regard were our studies of the stability of the potential

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energetic species cyclic N_3F and isomers of $(NO)_2$. In addition to their use in characterizing the limits of metastability of energetic materials these algorithms will have important impact on our ability to understand photochemical processes involved in atmospheric chemistry and consider one of the newly emerging 'hot' topics in molecular physics the importance of Berry's geometric phase in molecular processes.

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PUBLICATIONS

INVITED PUBLICATIONS

1. *Electronic Structure Aspects of Nonadiabatic Processes in Polyatomic Systems*
   D. R. Yarkony,in Modern Electronic Structure Theory, ed.. D. R. Yarkony (World Scientific, Singapore, 1995) .

2. *Molecular structure*
   D. R. Yarkony, in Atomic, Molecular and Optical Physics Reference Book, G. F. Drake, editor,to appear

JOURNAL ARTICLES

1. *Systematic Determination of Intersections of Potential Energy Surfaces Using a Lagrange Multiplier Constrained Procedure*
   David R. Yarkony, J. Phys. Chem. **97**, 4407 (1993)

2. *On the Intersection of Two Potential Energy Surfaces of the Same Symmetry: Systematic Characterization Using a Lagrange Multiplier Constrained Procedure*
   M. Riad Manaa and David R. Yarkony, J. Chem. Phys. **99**, 5251 (1993).

3. *Nonadiabatic Perturbations and Fine Structure Splittings in the $1,2^3\Pi_g$ States of B_2: An Analysis Based on Adiabatic and Rigorous Diabatic States*
   M. Riad Manaa and David R. Yarkony J. Chem. Phys. **100**, 8204 (1994)

4. *A Theoretical Treatment of the Radiative Decay of the ($a^3\Pi$, v, N, F_i, e/f) Levels of BH*
   Lisa A. Pederson, Hinne Hettema and David R. Yarkony, J. Phys. Chem. **98**, 11069 (1994).

5. *Radiationless Decay of the 1,2,3$^3\Pi_g$ States of Al_2: A Fully First Principles Treatment using Adiabatic and Rigorous Diabatic States*
Seungsuk Han, Hinne Hettema and David R. Yarkony, J. Chem. Phys. **102**, 1955 (1995)

6. *On the Spin-orbit induced Radiationless Decay of the $b^3\Sigma^-$ State of BH*
Lisa A. Pederson and David R. Yarkony, Mol. Phys. **84**,611(1995).

7. *Radiative and Radiationless Decay of Resonances Resulting from Electronically Nonadiabatic Interactions: A Computational Approach Valid for both Narrow and Broad Linewidths and Large Energy Shifts*
Seungsuk Han and David R. Yarkony , J. Chem. Phys. **103**, 7336 (1995)

8. *On the Structure and Stability of Geometrical Isomers of N_3F*
Galina Chaban, David R. Yarkony, Mark S. Gordon, J. Chem. Phys. **103**, 7893(1995)

9. *Radiative and Radiationless Decay of Multichannel Resonances Resulting from Electronically Nonadiabatic Interactions: A Computational Approach Valid for both Narrow and Broad Linewidths and Large Energy Shifts*
Seungsuk Han and David R. Yarkony, Molec Phys. accepted for publication

10. *Radiative and Nonradiative Decay of the BH($b^3\Sigma^-$) State:A Joint Experimental and Theoretical Study*
Xin Yang, Lisa Pederson, David R. Yarkony, and Paul J. Dagdigian, J. Phys. Chem. accepted for publication

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

A principal focus of this research program is the electronic structure aspects of nonadiabatic processes related to the stability and formation of high energy density materials(HEDMs). Also considered are nonadiabatic and relativistic effects that impact the detection of molecular species involved in HEDM or chemcial laser development. These studies are enabled by a unique system of electronic structure algorithms, the BROOKLYN programs, that provide advanced capabilities for the study of the electronic structure aspects of spin-forbidden and spin-allowed electronically nonadiabatic processes. These methods, which we believe *define* the state of the art in these areas, have permitted us to make significant contributions to the understanding of electronically nonadiabatic processes. Perhaps our most significant accomplishement in this grant period has been the development of algorithms for characterizing surfaces of intersection of two states of distinct spin-multiplcity or *two states of the same symmetry*. They complement our existing capabilities for determining the relevant intersurface couplings, the derivative couplings that couple states of the same spin-multiplicity and the spin-orbit and dipolar spin-spin interactions that couple states of distinct spin-multiplicity and will be of considerable value in studying the radiationless decay of energetic species. Of particular relevance in this regard are our studies of the stability of the potential energetic species cyclic N_3F and isomers of $(NO)_2$. In addition to their use in characterizing the limits of metastability of energetic materials these algorithms will have important impact on our ability to understand photochemical processes involved in atmospheric chemistry and consider one of the newly emerging 'hot' topics in molecular physics the importance of Berry's geometric phase in molecular processes.

TABLE OF CONTENTS

REPORT DEFINITION 1

SUMMARY 2

TECHNICAL REPORT 3

I. New Tools for Characterizing Nonadiabatic Processes 4

A. Characterization of Surfaces of Intersection of Two States of Distinct Multiplicity or Two States of the Same Symmetry Using Analytic Derivative Techniques

B. Nonadiabatic Radiationless Decay of Resonances 5

II. Applications 6

A. Spin-forbidden Radiationless Decay of Energetic Materials 6

(i) $N_3F(^1A') \rightarrow N_2(X^1\Sigma_g^+) + NF(X^3\Sigma^-)$

(ii) $N_2O_2(^1A_{1g})(D_{2h}) \rightarrow NO(X^2\Pi) + NO(X^2\Pi)$

B. Nonadiabatic Effects in Molecular Spectra 7

(i) The Spectra of the $1,2^3\Pi_g$ States of B_2

(ii) Radiationless decay of $B_2(1,2^3\Pi_g, v)$

C. Radiative Decay of Electronically Excited Metastable Species 9

(i) The Lifetime of $BH(a^3\Pi)$

D. Spectroscopic Identification of Chemical Species 10

(i) Radiationless decay of $BH(b^3\Sigma^-)$

III. FUTURE DIRECTIONS 10

REFERENCES 11

PUBLICATIONS 13

PERSONNEL 14

INVITED PRESENTATIONS 14

TECHNOLOGY TRANSFER 16

INTERACTIONS 16

REPORT DEFINITION

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SUMMARY

We have made considerable progress in our program to develop new computer algorithms for the study of spin-conserving and spin-nonconserving electronically nonadiabatic processes. We have completed development of algorithms for characterizing surfaces of intersection of two states of distinct spin-multiplcity or *two states of the same symmetry*. These algorithms determine the surface of intersection of two electronic potential energy surfaces for which a subset of the internuclear parameters are kept fixed and the remainder are optimized to reduce the energy of the point of intersection. These algorithms include an automated procedure for constructing the totally symmetric portion of the hessian matrix using divided differences of the appropriate analytically determined gradients. They complement our existing capabilities for determining the relevant intersurface couplings, the derivative couplings that couple states of the same spin-multiplicity, and the spin-orbit and dipolar spin-spin interactions that couple states of distinct spin-multiplicity, and will be of considerable value in studying the radiationless decay of energetic species. In addition to their use in characterizing the limits of metastability of energetic materials these algorithms will have important impact on our ability to understand photochemical processes involved in atmospheric chemistry and consider one of the newly emerging 'hot' topics in molecular physics the importance of Berry's geometric phase in molecular processes.

Our need to estimate the lifetime of metastable species has lead us to develop a nonperturbative computational approach to treat resonances attributable to nonadiabatic radiationless decay into several electronically distinct channels. Expressions for both the radiative and radiationless decay rates were developed and an alternative derivation of Fano's classic multichannel line shape formula was obtained.

Previously we investigated the stability of the potential energetic materials, a–N_2O_2. We showed that a–N_2O_2, *stable with respect to spin-allowed decay*, is in fact rapidly predissociated to N_2O + $O(^3P)$ via a spin-forbidden channel. We have continued our studies along these lines completing, in collaboration with M. Gordon at Iowa State University, a study of the spin-forbidden predissociation of the potential HEDM cyclic N_3F, $N_3F(1^1A') \rightarrow N_2(X^1\Sigma_g^+) + NF(X^3\Sigma^-)$. It was concluded that this system is stable with respect to spin-forbidden decay to the N_2 + $NF(X^3\Sigma^-)$ asymptote

The spectroscopy of small boron containing compounds is of consequence owing to the importance of boron as a fuel additive. Brazier of the Phillips Laboratory, has pointed out existence of significant nonadiabatic effects in the $1,2^3\Pi_g$ states of B_2 that complicate the analysis of the B_2 spectra, particularly the vibrational level dependencc of the fine structure interaction. Although the electronic states of B_2 had been the object of several high quality theoretical studies the nonadiabatic interactions had not been characterized. As part of this grant the vibrational level dependence of the fine structure splitting was determined.

The metastable $a^3\Pi$ state of BH is involved in a potentital energy transfer chemical laser, suggested by D. Benard, based on the $BH(A^1\Pi) \rightarrow BH(X^1\Sigma^+)$ electronic transition. The radiative lifetime of this species, attributable to the spin-forbidden transition $a^3\Pi \rightarrow X^1\Sigma^+$, is an important factor in the design of such a laser system. The lifetimes of the individual fine structure levels ($a^3\Pi$, v, N, F_i, e/f) were determined in a pure Hund's case (b) approximation. In all cases the ($a^3\Pi$, v, N, F_i, e/f) levels are long-lived with lifetimes longer than 10 s for N = 0 and v = 0,1,2,3.

Because of the potential role of $BH(a^3\Pi)$ in the above noted chemical laser system quantitative detection schemes are desirable. Laboratory detection of the $a^3\Pi$ state is based on $b^3\Sigma^- \rightarrow a^3\Pi$ laser induced fluorescence. In order for this transition to be used to characterize the $a^3\Pi$ state in a quantitative manner the radiative and radiationless decay rates of $BH(b^3\Sigma^-)$ are required. To this end the rates for the spin-allowed radiative transitions ($b^3\Sigma^-$, v, J) $\rightarrow a^3\Pi$ and the spin-orbit induced radiationless decay process $b^3\Sigma^- \rightarrow 1^3\Sigma^+$ were determined. It was found that predissociation of $BH(b^3\Sigma^-, v)$ is negligible up to v=2, where measureable predissociation exists. This research was performed in collaboration with P. J .Dagdigian's group at Johns Hopkins. This experimental-theoretical collaboration was served to enhance considerably the impact of this study.

TECHNICAL REPORT

The thrust of our research program is to develop computational techniques to determine the stability with respect to radiationless decay, of potential high energy density materials. These techniques are then to be applied to the study of chemically relevant systems. We are also concerned with spectroscopic analyses relevant to the characterzation and detection of energetic species. During the present performance period we have produced new tools for the study of

nonadiabatic processes. In addition to their use in studying to the stability of energetic materials these algorithms have potentially broad impact, including applications in atmospheric photochemistry and as a tool to consider one of the newly emerging 'hot' topics in molecular physics the importance of Berry's geometric phase in molecular processes. Below we discuss the most significant components of our current research effort including (IA) development of a computational methodology to characterize surfaces of intersection of two states of either, distinct spin-multiplicity or, the same overall symmetry, (IIA) the use of this methodology to consider, in collaboration with M. Gordon at Iowa State University, the possibility of spin-forbidden radiationless decay in the potential energetic material cyclic N_3F, (IIC) the radiative lifetime of $BH(a^3\Pi)$ an intermediate in a chemical laser system proposed by D. Benard, and (IID) the radiative and radiationless decay rates of $BH(a^3\Sigma^-)$ required for the quantitative detection of $BH(a^3\Pi)$ using the $b^3\Sigma^- \rightarrow a^3\Pi$ transition in laser induced fluorescence.

I. New Tools for Characterizing Nonadiabatic Processes

A. Characterization of Surfaces of Intersection of Two States of Distinct Multiplicity or Two States of the Same Symmetry Using Analytic Derivative Techniques

When considering the stability of an energetic species corresponding to a local minimum on the ground potential energy surface one must consider the possibility of radiationless decay induced by intersections with nominally excited potential energy surfaces. The straightforward procedure that has been used in the past to characterize surfaces of intersection initially determines the potential energy surfaces in question and then characterizes their intersections. We have developed[1,2] an algorithm that directly determines, that is without prior determination of the potential energy surfaces in question, surfaces of intersection of two states of distinct multiplicity or two states of the same symmetry using analytic derivative techniques.

The algorithm determines the solution of the following Newton-Raphson equations:

$$\begin{bmatrix} \mathbf{Q}^{IJ}(\mathbf{R},\xi,\lambda) & \mathbf{g}^{IJ}(\mathbf{R}) & \mathbf{h}^{IJ}(\mathbf{R}) & \mathbf{k}(\mathbf{R}) \\ \mathbf{g}^{IJ}(\mathbf{R})^{\dagger} & 0 & 0 & \mathbf{0} \\ \mathbf{h}^{IJ}(\mathbf{R})^{\dagger} & 0 & 0 & \mathbf{0} \\ \mathbf{k}(\mathbf{R})^{\dagger} & \mathbf{0}^{\dagger} & \mathbf{0}^{\dagger} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \delta\mathbf{R} \\ \delta\xi_1 \\ \delta\xi_2 \\ \delta\lambda \end{bmatrix} = - \begin{bmatrix} \mathbf{g}^{I}(\mathbf{R}) + \xi_1 \mathbf{g}^{IJ}(\mathbf{R}) + \xi_2 \mathbf{h}^{IJ}(\mathbf{R}) + \sum_{i=1}^{M} \lambda_i \mathbf{k}^{i}(\mathbf{R}) \\ \Delta E^{0}_{IJ}(\mathbf{R}) \\ 0 \\ K(\mathbf{R}) \end{bmatrix} \begin{matrix} 1.1\text{a} \\ 1.1\text{b} \\ 1.1\text{c} \\ 1.1\text{d} \end{matrix}$$

where ξ and λ are Lagrange multipliers, $\Delta E^0_{IJ}(\mathbf{R}) \equiv E^0_I(\mathbf{R}) - E^0_J(\mathbf{R})$, the $\mathbf{K}(\mathbf{R})$ are a set of geometrical constraints, $\delta\mathbf{R} = \mathbf{R}' - \mathbf{R}$, $\delta\lambda = \lambda' - \lambda$, $\delta\xi = \xi' - \xi$, $g^I_\alpha(\mathbf{R}) \equiv \dfrac{\partial E^0_I(\mathbf{R})}{\partial R_\alpha}$,

$g_\alpha^{IJ}(\mathbf{R}) \equiv \dfrac{\partial \Delta E_{IJ}^0(\mathbf{R})}{\partial \mathrm{R}_\alpha}$, $h_\alpha^{IJ}(\mathbf{R}) \equiv \mathbf{c}^{I\dagger}\dfrac{\partial \mathbf{H}(\mathbf{R})}{\partial \mathrm{R}_\alpha}\mathbf{c}^J$, $k_\alpha^i(\mathbf{R}) \equiv \dfrac{\partial K_i(\mathbf{R})}{\partial \mathrm{R}_\alpha}$ and $\mathbf{Q}^{IJ}$ is a matrix of second derivative terms. Implicit in the design of the algorithm based on this system of equations is the assumption that the gradients $h_\alpha^{IJ}(\mathbf{R})$, $g_\alpha^{IJ}(\mathbf{R})$ and $g_\alpha^I(\mathbf{R})$ are readily available. This is accomplished through the use of analytic gradient techniques.

Eq. 1.1a achieves the energy minimization. Eqs 1.1b,c enforce the requirement $E_I(\mathbf{R}) = E_J(\mathbf{R})$ while eq. 1.1d enforces the geometrical constraints, $\mathbf{K}(\mathbf{R}) = \mathbf{0}$. Efficient energy minimization requires the availability of the Hessian $\mathbf{Q}^{IJ}(\mathbf{R}, \boldsymbol{\xi}, \boldsymbol{\lambda})$. The $\mathbf{R}$, $\boldsymbol{\xi}$ contribution, $\mathbf{Q}^{IJ}(\mathbf{R}, \boldsymbol{\xi}, \mathbf{0})$ is currently obtained by divided difference

$$\mathbf{Q}^{IJ}(\mathbf{R}, \boldsymbol{\xi}, \mathbf{0}) = [(\mathbf{g}^I + \xi_1\mathbf{g}^{IJ} + \xi_2\mathbf{h}^{IJ})(\mathbf{R} + \varepsilon\mathbf{I}^\alpha) - (\mathbf{g}^I + \xi_1\mathbf{g}^{IJ} + \xi_2\mathbf{h}^{IJ})(\mathbf{R})]/\varepsilon \qquad 1.2$$

where $\mathbf{I}^\alpha$ is a unit vector in the direction R^α. The $\boldsymbol{\lambda}$ contribution to $\mathbf{Q}^{IJ}(\mathbf{R}, \boldsymbol{\xi}, \boldsymbol{\lambda})$ is readily evaluated analytically. The $\mathbf{I}^\alpha$ are usually taken to be atom centered cartesian coordinates, W_γ, where $W = X,Y,Z$, and $\gamma = 1 - M$ denotes the M atoms. However when spatial symmetry constraints are imposed use of eq. 1.2 for $\mathbf{I}^\alpha = W_\gamma$ is computationally inconvenient. These displacements do not preserve the point group symmetry, so that symmetry cannot be exploited in the evaluation of the electronic wavefunction. In addition when spatial symmetry is exploited the number of degrees of freedom that must be considered in the evaluation of eq. 1.2, a time consuming step, is reduced. An automated procedure has been implemented to evaluate eq. 1.2 with respect to the totally symmetric internal coordinates. This algorithm has been used to considerable advantage in the studies of cyclic N_3F discussed below.

B. Nonadiabatic Radiationless Decay of Resonances

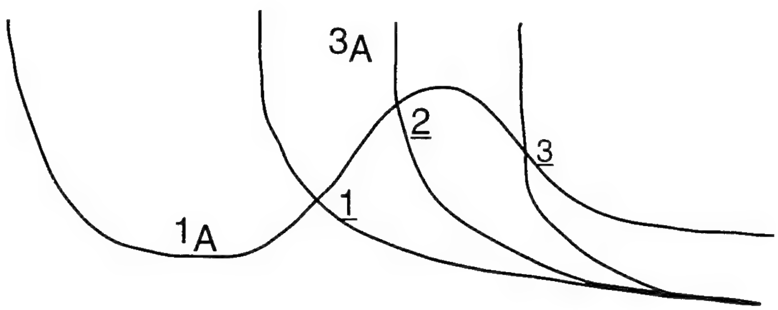
To faciliate our studies of radiationless decay diatomic systems a nonperturbative computational approach was developed to treat resonances attributable to nonadiabatic radiationless decay into several electronically distinct channels. Expressions for both the radiative and radiationless decay rates were developed and an alternative derivation of Fano's classic multichannel line shape formula [3,4] was obtained. Although the approach is nonperturbative the linewidth is expressed in a Golden rule type formula. The resonance energy is obtained from the iterative solution of an eigenvalue problem in the bound state space avoiding the tedious

characterization of the S-matrix as a function of scattering energy. These attributes enable efficient determination both narrow and broad linewidths and large resonance energy shifts.

II. Applications

A. Spin-forbidden Radiationless Decay of Energetic Materials

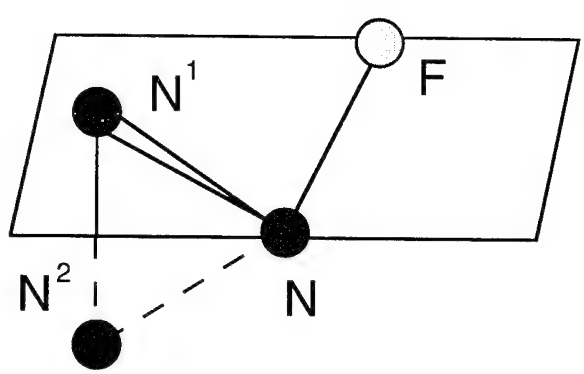
To address the question of spin-forbidden radiationless decay of an energetic material in a singlet electronic state the topology of the singlet - triplet surface of intersection is required. The range of situations that can arise is illustrated in the following figure:



where intersection 1 lies inside the barrier to spin-allowed dissociaton, intersection 3 lies behind that barrier and intersection 2 represents an intermediate case. In situation 3(1) the species will (not) be sufficiently long lived to be a potential HEDM species. In situation 2 careful consideration of the nonadiabatic dynamics will be required.

1. $N_3F(^1A') \rightarrow N_2(X^1\Sigma_g^+) + NF(X^3\Sigma^-)$

As part of an ongoing collaboration with Gordon's group at Iowa State University the $^1A'$ and $^3A''$ potential energy surfaces for the N3F molecule were studied using multi-configurational wave functions.[5] Two new isomers were found, one on the singlet ($^1A'$) and one on the triplet ($^3A''$) surface. Both isomers have a 3-membered cyclic structure and C_s symmetry. The singlet isomer is pictured below



The singlet cyclic isomer is endoergic relative to the open fluorine azide by 15-17 kcal/mol. Its kinetic stability is close to the stability of the open isomer: the barrier separating the cyclic isomer from the dissociation products $N_2(X^1\Sigma_g^+)$+NF $(a^1\Delta)$ is about 13-17 kcal/mol and is lower than the barrier to isomerization. The triplet cyclic isomer is much higher in energy (about 70 kcal/mol), with a barrier to dissociation to $N_2(X^1\Sigma_g^+)$+NF$(X^3\Sigma^-)$ on the order of 15 kcal/mol but can decay radiatively to the lower singlet surface. Crossings of the $^1A'$ and the $^3A''$ surfaces may allow the cyclic singlet isomer to predissociate to the ground state products, $N_2(X^1\Sigma_g^+)$+NF$(X^3\Sigma^-)$. It was shown, however, that the singlet-triplet surface of intersection lies 'behind' (intersection 3) the barrier to singlet decomposition, so that spin-forbidden predissociation will not preclude detection of cyclic N_3F.

(ii). $N_2O_2(^1A_{1g})(D_{2h}) \rightarrow NO(X^2\Pi) + NO(X^2\Pi)$

The geometric isomers of $(NO)_2$ have long been of interest to the HEDM program since Michels and Montgomery[6] first suggested a-N_2O_2 (NNOO) as a possible energetic material. Subsequently we showed that this isomer is *unstable* with respect to spin-forbidden radationless decay to N_2O + $O(^3P)$ (intersection 1).[7] Currently we, again in collaboration with Chaban and Gordon, are considering the stability of the D_{2h} form of N_2O_2, $(^1A_{1g})$. This species is metastable with respect to two $NO(X^2\Pi)$ and has a barrier to spin-allowed decay of approximately (MCSCF level) 47 kcal/mol. In this instance preliminary calculations suggest that a singlet- triplet crossing occurs inside the barrier to spin-allowed predissociation. Calculations are currently in progress to characterize the singlet-triplet surface of intersection.

B. Nonadiabatic Effects in the Spectra of HEDM Species

(i) The Spectra of the $1,2^3\Pi_g$ States of B_2

Our interest in B_2 has been stimulated the potential of boron containing compounds, as high energy density propellants.[8] Recently observation of five band systems of B_2[8] has been reported, including two bands involving the $1,2^3\Pi_g$ states, the $2^3\Pi_u - 1^3\Pi_g$ and the $2^3\Pi_g$ – $A^3\Pi_u$ bands. These studies benefitted from several high quality theoretical studies of this homonuclear diatomic molecule.[9-12] Despite the availability of high quality *ab initio* potential

energy curves and interstate electronic transition moments, detailed spectral analyses are hampered by the presence of nonadiabatic perturbations in the spectra. Of particular concern to our research are the $1,2^3\Pi_g$ states. Brazier and Carrick[8] observed significant deviations from the expected isotopomer relations in the $(2^3\Pi_g, v = 0) - (A^3\Pi_u, v = 0)$ band, deviations they attributed to perturbations in the $2^3\Pi_g$ state. On the basis of previous theoretical work[12] these perturbations are likely to result from an avoided crossing with the $1^3\Pi_g$ state. The avoided crossing of the $1,2^3\Pi_g$ states is expected to significantly effect the vibrational level dependence of the fine structure splitting constant in both these states. This quantity is of practical importance as the inference of the fine structure splitting constant was key to a recent assignment[8] of the $(2^3\Pi_u, v= 0) - (1^3\Pi_g, v = 0)$ band.

For these reasons nonadiabatic effects and fine structure splittings in the $1,2^3\Pi_g$ states of B_2 were studied. Adiabatic electronic wavefunctions $\Psi^a(J^3\Pi_g)$ were computed at the multireference configuration interaction level. The interstate derivative couplings $f^{IJ}(R) = \left\langle \Psi^a_{I^3\Pi_g}(\mathbf{r};R) \middle| \frac{d}{dR} \Psi^a_{J^3\Pi_g}(\mathbf{r};R) \right\rangle_{\mathbf{r}}$, $I=1$, $J=2$, were computed and used to construct 'rigorous' diabatic electronic states. The spin-orbit interactions responsible for the fine structure splitting in the $1,2^3\Pi_g$ states were determined. These electronic structure data were used to determine the vibrational structure of the $1,2^3\Pi_g$ states in both coupled adiabatic and coupled diabatic states bases. As a result of an avoided crossing of the $1,2^3\Pi_g$ states the fine structure splitting constants exhibit a marked geometry dependence. The fine structure splitting constants for the $(1^3\Pi_g, v = 0)$ and $(2^3\Pi_g, v = 0)$ levels were found to be $-4.2(-4.4)$[8], $1.37(1.54)$[13] cm^{-1}, respectively in good agreement with a recent experimental determinations given parenthetically.

(ii) Predissociation of the $1,2^3\Pi_g$ electronic states of B_2 - Work In Progress

Brazier and Carrick[13] observed a sharp cut off in the vibrational spectrum of the $2^3\Pi_g$ state of B_2 for $v > 1$. One of the goals of our current research effort is to extend the above study to provide a theoretical underpining for this observation.

To address this question the resonance theory of subsection IB is being used in conjunction with our capabilities to determine the derivative couplings $f^{IJ}(R)$ noted above . In

contradistinction to the above study however, here adiabatic electronic wavefunctions for three $^3\Pi_g$ states are required. This has been accomplished at the multireference configuration interaction level. The associated $f^{IJ}(R)$ were computed and used to construct 'rigorous' diabatic electronic states. These electronic structure data are being used to understand the mechanism of the predissociation of the ($2^3\Pi_g$, $v = 2$) level which in the adiabatic state approximation is a purely bound state but is not observed spectroscopically.[13]

C. Radiative Decay of Electronically Excited Metastable Species

(i) The Lifetime of BH($a^3\Pi$)

Benard *et. al*[14,15] have reported initial efforts toward the development of a chemical laser system based on the $A^1\Pi - X^1\Sigma^+$ transition in BH. BH($A^1\Pi$) is produced by energy transfer from the metastable $a^1\Delta$ state of NF, $T_e = 11442$ cm^{-1},[16] as follows, BH($X^1\Sigma^+$) + NF($a^1\Delta$) $\rightarrow$ BH($a^3\Pi$) + NF($X^3\Sigma^-$) and BH($a^3\Pi$) + NF($a^1\Delta$) $\rightarrow$ BH($A^1\Pi$) + NF($X^3\Sigma^-$). This work has stimulated our interest in the stability and detection(see below) of BH($a^3\Pi$). To this end the spin-forbidden radiative decay process BH($a^3\Pi$) $\rightarrow$ BH($X^1\Sigma^+$) was studied[17] using extended correlation consistent basis sets, second order configuration interaction wavefunctions and the Breit-Pauli spin-orbit approximation.[18] The two unique electronic transition moments, $\mu_\perp$ and $\mu_{||}$, connecting the $a^3\Pi$ and $X^1\Sigma^+$ nonrotating molecule states were determined. The lifetimes of the individual fine structure levels ($a^3\Pi$, v, N, F_i, e/f) were determined in a pure Hund's case (b) approximation. In all cases the ($a^3\Pi$, v, N, F_i, e/f) levels are long-lived with lifetimes longer than 10 s for N = 0 and v = 0,1,2,3.

D. Spectroscopic Identification of Chemical Species

(i) Radiationless decay of BH($b^3\Sigma^-$)

Laboratory detection of BH($a^3\Pi$) is based on $b^3\Sigma^- \rightarrow a^3\Pi$ laser induced fluorescence.[19] In order for this transition to be used to characterize the $a^3\Pi$ state in a quantitative manner the radiative and radiationless decay rates of BH($b^3\Sigma^-$) are required. To this end rates for the spin-allowed radiative transitions ($b^3\Sigma^-$, v, J) $\rightarrow$ $a^3\Pi$ (Ref. 17) and the spin-orbit induced radiationless decay process $b^3\Sigma^- \rightarrow 1^3\Sigma^+$ (Ref. 20) were determined. The spin-orbit coupling was determined

within the Breit-Pauli approximation using MCSCF/CI wavefunctions. The radiationless decay lifetimes of the ($b^3\Sigma^-$,v,N, F_i) fine structure levels were determined in a Hund's case (b) approximation. The ($b^3\Sigma^-$,v = 0 – 2, N = 0 – 15) levels are not significantly predissociated. However a spin-orbit induced perturbation $b^3\Sigma^- \sim 1^3\Sigma^+$ of magnitude approximately 0.2 cm^{-1} within the crossing region of the $b^3\Sigma^-$ and $1^3\Sigma^+$ states results in appreciable predissociation of the v' = 3 (v' = 2) level in BH for low N (high N).

These theoretical predictions were compared with lifetimes of rotational/fine-structure levels of electronically excited BH($b^3\Sigma^-$), in vibrational levels $v' = 0 - 4$, determined from fluorescence decay waveforms with laser excitation on isolated rotational lines in the $b^3\Sigma^- - a^3\Pi$ $\Delta v = 0$ sequence.[21] The experimental and theoretical lifetimes agree very well. This comparison confirms that the low $b^3\Sigma^-$ rotational levels for $v' = 0 - 2$ decay purely radiatively, with a rate decreasing as v' increases. These rates are virtually independent of the fine-structure level. However the lifetimes of the higher vibrational levels exhibit significant fine-structure level dependence, with the shortest values obtained for the F_2 levels. This behavior was shown to be attributable to predissociation induced by $b^3\Sigma^- \sim 1^3\Sigma^+$ spin-orbit coupling.

III Future Directions

(i) Prediction of MCD Spectra

The characterization of the local structure of first row elements in hydrogen matrices is an important problem in the study of cryogenic propellants. Magnetic circular dichroism (MCD) is one of the tools currently being used to investigate the problem. We are in the process of developing algorithms to calculate MCD spectra from first principles. As discussed in detail on our renewal proposal, our principle methodological advance involves the key B-term. We will replace the traditional, but computationally intractable, sum over states (the K-sum)

$$B(\mathrm{I}\rightarrow\mathrm{J}) = \quad \mathrm{Im}\sum_{\lambda',\lambda,K\neq J}\left\langle\Psi^e_{I_{\lambda'}}\middle|\boldsymbol{\mu}\middle|\Psi^e_{J_\lambda}\right\rangle\times\left\langle\Psi^e_{I_{\lambda'}}\middle|\boldsymbol{\mu}\middle|\Psi^e_{K}\right\rangle\cdot\left\langle\Psi^e_{J_\lambda}\middle|\boldsymbol{m}\middle|\Psi^e_{K}\right\rangle/\Delta E_{KJ} \; +$$
$$\mathrm{Im}\sum_{K\neq A,\lambda,\lambda'}\left\langle\Psi^e_{I_{\lambda'}}\middle|\boldsymbol{\mu}\middle|\Psi^e_{J_\lambda}\right\rangle\times\left\langle\Psi^e_{J_\lambda}\middle|\boldsymbol{\mu}\middle|\Psi^e_{K}\right\rangle\cdot\left\langle\Psi^e_{K}\middle|\boldsymbol{m}\middle|\Psi^e_{I_{\lambda'}}\right\rangle/\Delta E_{KI}$$

with a direct solution of a system of linear equations

$$B(\mathrm{I}\to\mathrm{J}) = \mathrm{Im}\sum_{\lambda,\lambda'}\left\langle \Psi^{e}_{I_{\lambda'}}\middle|\boldsymbol{\mu}\middle|\Psi^{e}_{J_{\lambda}}\right\rangle \times \left\langle \Psi^{e}_{I_{\lambda'}}\middle|\boldsymbol{\mu}\cdot\bar{\Psi}^{1-m}_{J_{\lambda}}\right\rangle + \mathrm{Im}\sum_{\lambda,\lambda'}\left\langle \Psi^{e}_{I_{\lambda'}}\middle|\boldsymbol{\mu}\middle|\Psi^{e}_{J_{\lambda}}\right\rangle \times \left\langle \Psi^{e}_{J_{\lambda}}\middle|\boldsymbol{\mu}\cdot\bar{\Psi}^{1-m}_{I_{\lambda'}}\right\rangle$$

where

$$\left(H - E_{J_{\lambda}}\right)\bar{\Psi}^{1-m}_{J_{\lambda}} = Q_{A}\mathbf{m}\Psi^{e}_{J_{\lambda}} \qquad .$$

This work will support an AFOSR funded experimental program in Professor Kenney's laboratory.

(ii) Pathways to energetic species

Conical intersections of two states of the same symmetry provide efficient pathways for electronically excited states to decay radiationlessly to the ground electronic state. The barriers that 'protect' metstable structures suggest the nearbye presence of conical intersections with excited states. These conical intersections, funnels, may provide pathways to the metastable structures (stabilized by collisions) that represent HEDM species. While certainly not a viable synthetic route for large quantities of such a material these pathways would allow for the experimental study of such systems. The algortihms describe above will be used to consider this possibility.

REFERENCES

1 D. R. Yarkony, *J. Phys. Chem* **97,** 4407-4412 (1993).

2 M. R. Manaa and D. R. Yarkony, *J. Chem. Phys.* **99,** 5251 (1993).

3 U. Fano, *Phys. Rev.* **124,** 1866 (1961).

4 U. Fano and J. W. Cooper, *Phys. Rev* **137,** A1364-A1379 (1965).

5 G. Chaban, D. Yarkony, and M. Gordon, (1995).

6 H. H. Michels and J. A. Montgomery Jr., *J. Chem. Phys.* **88,** 7248 (1988).

7 K. A. Nguyen, M. S. Gordon, J. A. Montgomery, H. H. Michels, and D. R. Yarkony, *J. Chem. Phys.* **98,** 3845 (1993).

8 C. R. Brazier and P. G. Carrick, *J. Chem. Phys.* **96,** 8683 (1992).

9 P. J. Bruna and J. S. Wright, *J. Mol. Struct. (Theochem)* **210,** 243 (1990).

10 P. J. Bruna and J. S. Wright, *J. Chem. Phys.* **91,** 1126 (1989).

11 S. R. Langhoff and C. W. Bauschlicher, *J. Chem. Phys.* **95,** 5882 (1991).

12 M. Hachey, S. P. Karna, and F. Grein, *J. Phys. B.* **25,** 1119-1136 (1992).

13 C. R. Brazier and P. G. Carrick, *J. Chem. Phys.* **100,** 7928 (1994).

14 D. J. Benard, in *Abstracts of the High Energy Density Materials Contractors Meeting* (Air Force Office of Scientific Research, Cal-Neva Lodge, Nevada, 1993).

15 D. J. Benard, E. Boehmer, H. H. Michels, and J. J. A. Montgomery, *J. Phys. Chem.* **98,** 8952-8958 (1994).

16 K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

17 L. A. Pederson, H. Hettema, and D. R. Yarkony, *J. Phys. Chem* **98,** 11069-11074 (1994).

18 H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Plenum/Rosetta, New York, 1977).

19 X. Yang and P. J. Dagdigian, *J. Phys. Chem.* **97,** 4270 (1993).

20 L. A. Pederson and D. R. Yarkony, *Molec. Phys.* **84,** 611 (1995).

21 X. Yang, L. Pederson, D. R. Yarkony, and Paul J. Dagdigian, *J. Phys. Chem.* (1996).

PUBLICATIONS

INVITED PUBLICATIONS

4. *Electronic Structure Aspects of Nonadiabatic Processes in Polyatomic Systems*
D. R. Yarkony,in Modern Electronic Structure Theory, ed.. D. R. Yarkony (World Scientific, Singapore, 1995).

5. *Molecular structure*
D. R. Yarkony, in Atomic, Molecular and Optical Physics Reference Book, G. F. Drake, editor,to appear

JOURNAL ARTICLES

††78. *Systematic Determination of Intersections of Potential Energy Surfaces Using a Lagrange Multiplier Constrained Procedure*
David R. Yarkony, J. Phys. Chem. **97**, 4407 (1993)

††80. *On the Intersection of Two Potential Energy Surfaces of the Same Symmetry: Systematic Characterization Using a Lagrange Multiplier Constrained Procedure*
M. Riad Manaa and David R. Yarkony, J. Chem. Phys. **99**, 5251 (1993).

††83. *Nonadiabatic Perturbations and Fine Structure Splittings in the* $1,2^3\Pi_g$ *States of* B_2*: An Analysis Based on Adiabatic and Rigorous Diabatic States*
M. Riad Manaa and David R. Yarkony J. Chem. Phys. **100**, 8204 (1994)

††85. *A Theoretical Treatment of the Radiative Decay of the* $(a^3\Pi, v, N, F_i, e/f)$ *Levels of BH*
Lisa A. Pederson, Hinne Hettema and David R. Yarkony, J. Phys. Chem. **98**, 11069 (1994).

††87. *Radiationless Decay of the* $1,2,3^3\Pi_g$ *States of* Al_2*: A Fully First Principles Treatment using Adiabatic and Rigorous Diabatic States*
Seungsuk Han, Hinne Hettema and David R. Yarkony, J. Chem. Phys. **102**, 1955 (1995)

††88. *On the Spin-orbit induced Radiationless Decay of the* $b^3\Sigma^-$ *State of BH*
Lisa A. Pederson and David R. Yarkony, Mol. Phys. **84**,611(1995).

†90. *Radiative and Radiationless Decay of Resonances Resulting from Electronically Nonadiabatic Interactions: A Computational Approach Valid for both Narrow and Broad Linewidths and Large Energy Shifts*
Seungsuk Han and David R. Yarkony , J. Chem. Phys. **103**, 7336 (1995)

91. *On the Structure and Stability of Geometrical Isomers of* N_3F
Galina Chaban, David R. Yarkony, Mark S. Gordon, J. Chem. Phys. **103**, 7893(1995)

92. *Radiative and Radiationless Decay of Multichannel Resonances Resulting from Electronically Nonadiabatic Interactions: A Computational Approach Valid for both Narrow and Broad Linewidths and Large Energy Shifts*

Seungsuk Han and David R. Yarkony, Molec Phys. accepted for publication

94. *Radiative and Nonradiative Decay of the BH($b^3\Sigma^-$) State:A Joint Experimental and Theoretical Study*
Xin Yang, Lisa Pederson, David R. Yarkony, and Paul J. Dagdigian, J. Phys. Chem. accepted for publication

†† Reprint previously provided
† Reprint included with this report.

PERSONNEL

The following scientists have contributed to work performed during the course of this grant.

Graduate Student

Ms. Lisa Pederson

Postdoctoral Research Associates:

Dr. M. Riad Manaa
Dr. Hinne Hettema
Dr. Seungsuk Han

Principal Investigator

Professor David R. Yarkony

INVITED PRESENTATIONS

The following invited presentations were given by the principal investigator based on work performed during the course of this grant:

Named Lectureships

1994 Robert S. Mulliken Lectures(shared with Alex Dalgarno)
Nonadiabatic Chemistry: A Theoretician's Perspective
presented at Center for Computational Quantum Chemistry
Univeristy of Georgia
June 3, 1994

Invited Talks

Nonadiabiatic Effects in Electronic Spectra
presented at *48th Ohio State University International Symposium on Molecular Spectroscopy*
Ohio State University
Columbus, Ohio
June 14-18, 1993

Nonadiabatic Chemistry: New Theoretical Perspectives

presented at Department of Chemistry
UC Irvine
March 10, 1994

Nonadiabatic Processes Relevant to the Stability and Detection of High Energy Density Materials

presented at HEDM Contractors Meeting
Cal-Neveda Lodge
Reno, Neveda
June 5, 1994

Characterization of Surfaces of Intersection in Polyatomic Systems: Methods and Applications

presented at 8th International Congress of Quantum Chemistry
Prague, Czech Republic
June 19-23, 1994

Conical Intersections of two states of the same symmetry and photodissociation in polyatomic systems

presented at Workshop on:Electronically nonadiabatic processes in chemical dynamics, spectroscopy and electronic structure
Chemistry Division (Building 200)
Argonne National Laboratory
July 20-23, 1994

Nonadiabatic Chemistry: New Theoretical Perspectives

presented at: ACS 208th National Meeting
Washington DC,
August 1994

Nonadiabatic Chemistry: New Theoretical Challenges

presented at: University of Chicago
Department of Chemistry,
January 17 1995

Determination of Conical Intersections and Derivative couplings for large scale configuration interaction wavefunctions-Methods and applications

presented at: Workshop on Geometric Phases in Atomic and Molecular Physics
University of Neveda, Las Vegas,
February 1, 1995

Nonadiabatic Processes: New Computational Challenges

presented at: University of Connecticut
Department of Physics,
February 10, 1995

Nonadiabatic Chemistry: New Computational Challenges

presented at: Iowa State University

Department of Chemistry,
March 31, 1995

Nonadiabatic Chemistry: NewTheoretical Challenges

presented at: Cal Tech
Department of Chemistry,
May 2, 1995

Nonadiabatic Chemistry: NewTheoretical Challenges

presented at: State University of Leiden
Gorlaeus Laboratory
Leiden, The Netherlands
July 6, 1995

TECHNOLOGY TRANSFER

Radiative and Radiationless decay rates of $b^3\Sigma^-$ state of BH

D. J. Benard, Ellen Boehmer
Science Center, Rockwell International Corp.
and
C. R. Brazier and P. G. Carrick
Phillips Laboratory, Edwards AFB

Transfer: To quantify conditions in a laser system LIF may be used a probe. In order to be a quantitative probe the radiative AND radiationless decay rates of the laser excited state must be known. Lisa Pederson calculated the radiative decay rate for the $b^3\Sigma^- \rightarrow a^3\Pi$ transition (Pub. 85) and the decay rate for the radiationless transition $b^3\Sigma^- \sim 1^3\Sigma^+$ (Pub. 88) in BH. These results were communicated by Ms Pederson to E. Boehmer. This information is needed to determine BH($a^3\Pi$, v) level populations by LIF. BH($a^3\Pi$) is an energetic intermediate in a potential laser system being considered by Rockwell.
We have communicated the results of our combined experimental/theoretical treatment [Pubs. 88 and 94] of the decay of the $b^3\Sigma^-$ state to C. Brazier of the Phillips Laboratory, Edwards AFB. This will interaction will be useful in understanding Brazier's measured spectra of BH $b^3\Sigma^-$.

Comments: The capability to determine spin-allowed radiative decay rates is routine in groups specializing in electronic structure theory. However the capability to quantify the *spin-orbit* induced radiationless decay process $b^3\Sigma^- \sim 1^3\Sigma^+$ is not. Our capabities define the state of the state in this area and have important applications in various processes of interest to the Air Force .

INTERACTIONS

C. R. Brazier and P. G. Carrick
Phillips Laboratory, Edwards AFB

We have performed a theoretical analysis of the vibrational level dependence of the fine structure splitting constant in the $1,2^3\Pi_g$ states of B_2. This analysis required the determination of nonadiabatic interactions, derivative couplings, between the $1,2^3\Pi_g$ adiabatic states as well is the spin-orbit interactions. We are currently extending this work to include predissociation of the $1,2^3\Pi_g$ states. This work [Pub. 83 and work in progress] was/will be communcated to Brazier and Carrick and supports their spectroscopic studies of these states.

Comments: The capability to determine the requisite potential energy curves is routine in groups specializing in electronic structure theory. However the capability to quantify the nonadiabatic (derivative) couplings is not. Again our capabilities define the state of the art in this area.